# COMMERCIAL PRODUCTION OF NITRATION GRADE TOLUENE FROM PETROLEUM.

BY
Walter Lawrence Prehn

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# COMMERCIAL PRODUCTION OF NITRATION GRADE TOLUENE FROM PETROLEUM

A Thesis
Presented to the Faculty of the Graduate School of Cornell
University for the Degree of
Master of Science in Engineering

By

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# BIOGRAPHICAL SKETCH

The writer was born in St. Louis, Missouri, 15 April 1920, and lived there and in Kansas City, Missouri, for six years before he moved with his family to Dallas, Texas.

He received his elementary training at the Armstrong School and his secondary training at the Highland Park High School in Dallas. He attended The Rice Insitute at Houston, Texas, from which he received the degree of Bachelor of Science in Chemical Engineering in April, 1943.

Immediately upon graduation from The Rice Institute, he went on active duty with the Naval Reserve, serving eighteen months in the Marshall Islands. He returned to the United States to enter the United States Naval Academy postgraduate course in Ordnance Engineering (Explosives) at Annapolis. The extension of this course is now in progress at Cornell University.

## INTRODUCTION

Before the entrance of the United States into World War II, nitration-grade toluene (99+% toluene) was obtained in relatively small quantities from numerous coke-oven operations throughout the country.(20) Because this production was a by-product related to the mining and utilization of coal, it was impossible economically and quickly to increase to increase the quantity of toluene from this source. The entire integrated process for making synthetic nitration-grade toluene from petroleum had been worked out by 1940.(10) The Baytown, Texas, refinery of The Humble Oil and Refining Company was the first plant to produce synthetic nitration-grade toluene on a commercial scale from petroleum. In the year after Pearl Harbor, this refinery supplied over half of the toluene used in America to make trinitrotoluene (TNT).

The toluene production before World War I was less than a million gallons annually (U. S. Bureau of Mines data) since by-product coking was practiced to a limited extent only. By 1918 the production was almost nine million gallons per year. In the year after World War I, production dropped to one or two million gallons annually and then rose steadily until it was about thirty million gallons for 1940.

Crude petroleum of the type available during World War II contains roughly half of one per cent of toluene, although the content of some crudes is as high as one or two per cent. To provide the necessary nitration-grade toluene above that available from the coal-tar industry, by extracting the natural toluene present in petroleum crudes, it would be necessary to process in a special manner nearly one-third of all the crude naphtha produced in this country. Therefore, the production of synthetic toluene seemed the only promising alternative.

To bridge the gap between the pre-war supply of toluene from the coal-tar industry and the demand for over two hundred million gallons required annually for war-time operations, the catalytic hydroforming process, developed by Standard Oil of New Jersey and the M. W. Kellogg Company in peacetime primarily for the desulfurization and octane improvement of motor gasolines, was immediately available for the production of synthetic toluene from selected petroleum fractions.
The cracked products of the older Dubbs and other thermal cracking units were not very high in aromatic content and therefore did not lend themselves to the further production of toluene on an economical basis. The cracked products from catalytic cracking chambers, on the other hand, can be made rich in aromatics by suitably adjusting the cracking conditions.

These are the only large scale sources of toluene today.

## NATURE OF TOLUENE(24)

Toluene, or toluol, is methyl benzene or phenyl methane. It is a colorless, inflammable liquid with a high refractive index. As an aromatic hydrocarbon, it has excellent anti-knock properties. Its boiling point is variously described as being between 110.3° and 110.6° C, while its freezing point is - 92.4° C. Toluene has a molecular weight of 92.06 and its specific gravity is 0.8708.

Toluene resembles benzene in many ways, although it differs from it somewhat in combustion phenomena at high pressures. Presence of a side chain in the toluene nucleus facilitates oxidation, but also gives rise to complications due to its simulataneous oxidation with the nucleus. Thus it has been found that benzyl alcohol, benzaldehyde and benzoic acid are formed as the result of a side-chain oxidation, together with 2 - 4 dihydroxy toluene and other aromatic dihydroxy derivatives.

Toluene differs from benzene in that there is a well defined induction period preceeding reaction and it is easier to control subsequent oxidation to produce considerable quant-

ities of one or the other intermediate products. For example, high pressure, together with the excess of the hydrocarbon, favor survival of the alcohol, while a progressive increase in the oxygen concentration causes the reaction to proceed at first mainly to the aldehyde stage and then to benzoic acid. By careful control it is found possible, even in the static system, to obtain yields of aromatic derivatives representing more than seventy per cent of the toluene consumed.

## OCCURRENCE OF TOLUENE IN PETROLEUM

Toluene is present as such in some crude petroleums, and can be recovered directly by distillation. The non-waxy, high-gravity crudes of Borneo have a high aromatic content. Benzene, toluene and higher homologs, naphthalene derivatives, cyclic hydrocarbons, decaline and tetraline are present. The crudes contain about equal parts of aromatics (largely toluene), naphthalenes and paraffins. The toluene fraction of Borneo crude was used for manufacture of TNT during World War I not only in England, but also in France, Holland and Germany. As early as 1906, it had been discovered, that the volatile fractions (35° - 60° C) of Borneo crude contained also naphthalenes and unusually large quantities of aromatic

hydrocarbons, amounting to as much as forty per cent and identified as benzene, toluene and meta xylene. At first this high aromatic content rendered the Borneo crude of low commercial value, but later it proved to be of greatest importance to the British Empire as a source for toluene for the Portshead TNT plant. The Borneo crude imported into England at that time had a specific gravity of 0.783; twenty per cent distilled below 100° C. The crudes contained seven per cent of benzene, fourteen per cent of toluene, fifteen per cent of xylenes and four percent of higher aromatics.

A similar ratio of benzene, toluene and xylene exists in the aromatic hydrocarbon content of some Iranian crudes. Some Rumanian crudes are also rich in aromatics.

Compounds present in crude naphtha can be classified as paraffins, naphthenes (cyclic paraffins) and aromatics. Naphthenes may contain rings of either five or six carbon atoms. For many years it has been known that with the aid of dehydrogenation catalysts, naphthenes containing six carbon atoms in the ring and normal paraffins could be converted to aromatics, but processes using these catalysts had never become commercial because the catalysts rapidly became inactivated by fouling and coke deposition. Table I, page 7,

gives the toluene and methyl cyclohexane contents of representative American crudes. The volume per cent of methyl cyclohexane reported includes also ethyl cyclopentane. Indi-

TABLE I[10]

Toluene and methyl cyclohexane plus ethyl cyclopentane contents of representative American crudes (volume per cent)

| Crude | Toluene | MCH |
|---|---|---|
| Texas Coastal | 0.03 | 1.2 |
| Conroe | 2.00 | 2.5 |
| East Texas | 0.40 | 1.7 |
| Kettleman Hills | 0.70 | 2.1 |
| Midway Light | 0.02 | 0.52 |
| North Sweden Mixture | 0.80 | 3.7 |
| Panhandle | 0.22 | 2.3 |
| Pecos | 0.03 | 1.0 |
| Refugio | 0.26 | 2.9 |
| Salt flat regions | 0.19 | 1.5 |
| Santa Maria | 0.15 | 0.79 |
| Sugarland | nil | 1.0 |
| Tomball Mixture | 1.10 | 2.1 |
| Tensley | 0.08 | 0.65 |
| West Texas | 0.50 | 1.3 |

cations are that ethyl cyclopentane may comprise between fifteen and twenty per cent of the total methyl cyclohexane (MCH) ethyl cyclopentane (ECP) mixture.(10) This table will be referred to later in connection with the discussion of methyl cyclohexane as source of toluene.

## PRODUCTION SOURCES

Since straight thermal cracking gives only very low yields of toluene, it has little importance as a source of this material. Toluene from petroleum is made by catalytic cracking. The catalytic process may be classified into fixed-bed and moving-bed reactions. To the former class belong the older Houdry process, the newer hydroforming process, cycloversion and various other minor variations of these. To the latter class belong two new processes known respectively as the thermofor catalytic cracking (TCC) process and the fluid catalyst process.

The first commercial catalytic cracking plant was placed on stream at the Paulsboro, New Jersey, refinery of the Socony Vacuum Oil Company, in 1936, using the Houdry process. This was the only catalytic cracking process in commercial operation when the United States entered World War II. Of the three major catalytic cracking processes (Houdry, fluid and TCC) the Houdry process represents some twenty-nine per cent of the total catalytic chamber volume, while the fluid process represents fifty per cent and the thermofor process, thirty-one per cent.(1) The cycloversion, thermofor and fluid processes all reached commercialization after Pearl Harbor.

The many methods which have been described in the literature for the manufacture of toluene represent a wide coverage of the field of synthetics. Such methods, other than those discussed above, include the dehydrogenation of relatively pure methyl cyclohexane(13, 16, 19), the simultaneous dehydrogenation and cyclization of normal heptane(3, 5, 7, 8, 9, 14, 17, 18, 19, 32), the mixing of methane and benzene in the presence of catalysts at high temperatures and pressures(22), the treatment of pthalic acid or pthalic anhydride with hydrogen at raised temperatures and pressures in the presence of catalysts(26), the formation of toluene and other liquid hydrocarbons from acetylene which has been subjected to pyrogenetic conversion in the presence of hydrogen(15), and many others.

A brief discussion of the more important catalytic processes is given below, followed by a brief resumé of some of the various catalysts used.

## THE HOUDRY CATALYTIC CRACKING PROCESS (2, 6, 21)

The Houdry process first came to general notice when a former French watchmaker, Eugene Houdry, and his associates presented a paper on the catalytic processing of hydrocarbons before the November, 1938, meeting of the American Petroleum Institute. Previous to this announcement, the process had gone through a long period of development, dating back to as early as 1924. The first commercial plant using the Houdry process was put into production at the Paulsboro, New Jersey, refinery of the Socony Vacuum Oil Company in 1936.

The Houdry Catalytic Cracking process involves merely the passing of hydrocarbons through a fixed catalyst bed contained in the so-called catalyst or reaction "cases". This processing of the hydrocarbons is usually performed in the vapor phase, although this is not necessary. The Houdry process is based on three groups of interrelated inventions. These comprise, first, the catalysts themselves (discussed later, see "Catalysts", page 54), second, the apparatus in which the crude stock and the catalyst are brought into contact, and third, the methods and manipulations by which the catalyst reaction is induced and controlled. The commercial success of the process depends on the proper functioning of

the catalyst, the reaction vessels and the controls.

Actually, catalytic research had been increasing on a wide scale until 1931 when most petroleum interests were trying to find a catalytic method to replace the thermal cracking processes which were rather wasteful,$^{(25)}$ but the solving of the main problems by Eugene Houdry opened up the field for later advances. The basic principles of Houdry's original design were not changed until after the beginning of World War II and the subsequent acceleration of research. Until the Houdry process was placed in operation, the problem of catalyst regeneration had not been successfully solved.

The Houdry process involves passing a stream of hot hydrocarbon vapor, with a small amount of steam to assure the maintaining of the vapor mixture above its dew point in the reactor cases, through the catalyst cases, collecting and separating the catalyzed products and regenerating the catalyst when its activity has begun to drop. Simple as it may sound, this operation presented serious mechanical and constructional difficulties. The circumstances to which a Houdry catalyst case must conform are exacting. For efficient cracking the oil vapors enter the reactor cases at a temperature of about 840° F. During the cracking, carbonaceous deposits accumulate. These

must be burned off at a temperature above 950° F by passing a current of hot air through the cases. The change from cracking to regeneration may be in a period as short as five minutes. Very careful design is required to build a case that can withstand these rapid and severe fluctuations in temperature.

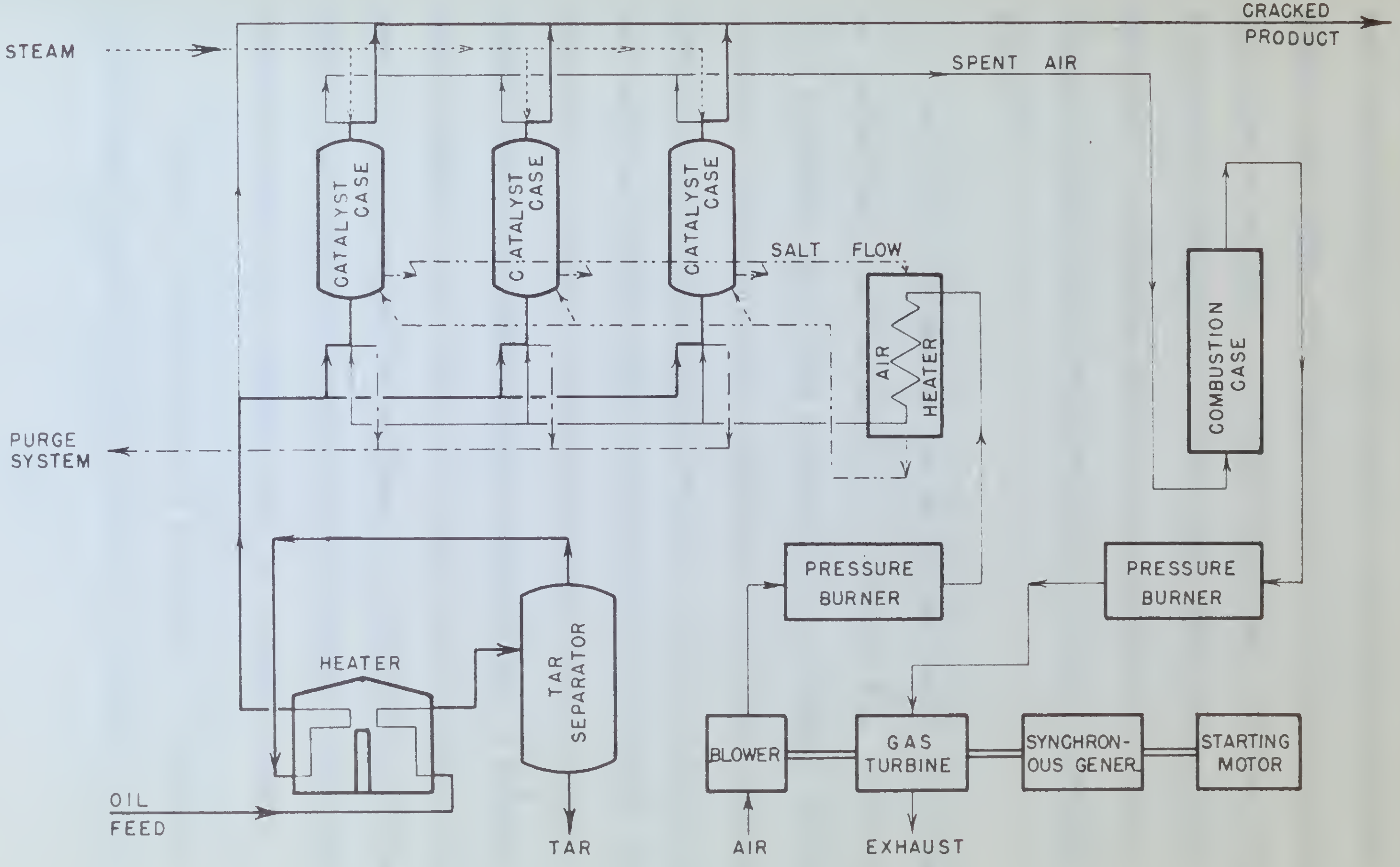
Even this was a relatively minor problem. The reaction is endothermic and therefore requires external heating while the case is on stream; the regeneration is exothermic and a large amount of heat must be dissipated to protect the catalyst. Since the catalyst itself is a relatively poor conductor of heat, an elaborate system of cooling vanes is placed inside the catalyst mass in the cases. These are so designed that at no point is the catalyst more than about one inch away from a vane surface. These vanes are supported on pipes through which flows a mixture of forty per cent sodium nitrite, seven per cent sodium nitrate and fifty-three per cent potassium nitrate. This acts as the heat-controlling medium. The apparatus for circulating the oil feed, the regenerating air and the heat controlling medium is constructed with the one thought of effecting the most rapid possible heat exchange.

Figure 1 on page 15 is the flow sheet of an early, simple Houdry cracking unit. The heavy lines trace the path of the crude oil feed through the catalyst cases to the finished cracked product. The dotted line is the steam line, while the dashed and dotted lines are the fused salt flow (— — ••) lines and the purge system (- •). The fine solid line indicates the flow of regeneration air through the plant.

After being heated in a furnace, the feed oil is charged to a tar separator. The oil is flashed in the tar separator into which the hot oil vapors are fed tangentially so that the tar may be removed by centrifugal action as well as by settling. The vapors from the tar separator are reheated and mixed with a little superheated steam to insure that they will be above their dew point before going to the cracking cases.

There are usually about twelve cracking cases, with two always attached in parallel. Thus they are connected in two groups of six cases, each group having its own inlet and outlet manifolds. One operating scheme is for each pair of cases to have an on-stream period of ten minutes. The valving system is arranged so that a pair of cases comes on stream every five minutes. This assures that a uniform flow of oil

FIGURE 1



HOUDRY CATALYTIC CRACKING PLANT

is entering and leaving the cases. The necessary valving is done automatically by motor-operated valves controlled by a single cycle timer. The vapors enter the bottom of the cases and leave at the top. The outlet vapors are conducted through a series of heat exchangers (not shown) where they give up their heat to incoming feed or air, and are then further treated by some method of recovery (see "Toluene Recovery", page 47).

The salient feature of the Houdry process is the catalyst or reactor case, and the method of operating it. These features distinguish the Houdry process from the thermal cracking process. The cases usually run about thirty-eight feet high and are ten or eleven feet in diameter. They are constructed as towers and contain tubes and flanges for conducting heat. One series of tubes is for the alternate passage of oil vapors and the air necessary for regeneration. A second series conducts the catalyzed oil vapors and the regeneration gases to their respective outlets. A third series of tubes carries the molten salt used for heat exchange. This salt loses its heat to the incoming air, as explained later.

A typical operation cycle is as follows. Utilizing a thirty-minute cycle, each case spends ten minutes on stream

while the oil vapors are being passed through for catalysis, five minutes for purging the case of oil vapors in preparation for regeneration (the oil vapors lost are recovered elsewhere in the plant and recycled), ten minutes for the complete regeneration operation and five minutes for purging the case of air and combustion products in preparation for resumption of catalysis. It is necessary to remove the hot oil vapors before admitting air at a burning heat, and to remove air before admitting oil vapors to avoid any chance of back firing. The purging in each case is done by a barometric vacuum system.

The regeneration with air is one of the most interesting features of the Houdry process. As may be noted from the flow sheet (Figure 1), air is forced by a blower through a heat exchanger where it picks up sufficient heat from the molten salt to oxidize the carbonaceous deposit on the catalyst rapidly. Upon issuing from the cases, the air passes through one or more combustion cases where combustion of carbon monoxide is completed. Later developments in the Houdry process eliminate these combustion cases, which contain a catalyst which reduces the oxidation temperature and allows some of the heat to be recovered. After passing through the combustion cases, the hot gases pass through a turbo-compressor unit. On arrival at the

air turbine of the turbo-compressor unit the hot gases, at about forty-five pounds per square inch pressure, are expanded to atmospheric pressure; in so doing they generate enough power to operate the initial air blower and also a synchronous generator which converts the excess energy into electric power. This use of a turbo-compressor reduces operating expenses considerably. The power generated is in excess of the electrical power required to operate the entire Houdry plant. For starting the plant, a starting motor is provided together with pressure burners in the air line before and after the catalyst cases, to provide the necessary starting heat.

There have been many improvements on the original Houdry design, the latest and most important of which is the adiabatic operating process which utilizes part of the heat generated during the combustion of the carbonaceous deposit on the catalyst more efficiently. The process is not fully adiabatic and the heat balance is not as precise as this thermodynamic term implies.

In the catalytic operations described above, the temperature in the reactor is held at about 825° F to 850° F. About twenty per cent of this heat is utilized for heat reaction during the cracking period, while eighty per cent

is absorbed by the molten salt. In the adiabatic process, a somewhat higher temperature is maintained. No molten salt is circulated, thus effecting a considerable saving in equipment and operating costs. The required amount of exothermic regeneration heat is stored in the mass of catalyst itself to be available for cracking the oil vapors. Part of the heat is removed in the air stream and used for steam and power generation, while the largest portion is carried away in the oil vapors leaving the catalyst case and is used to preheat the incoming feed. The catalyst cycle is the same for all Houdry processes, the adiabatic process differs from the normal operation only in the manner in which the heat is applied.

Advantages of the Houdry process over the previously used thermal cracking methods are that the Houdry process is far more flexible, it gives consistently high once-through yields of gasoline from any crude feed stock, it gives a gasoline with unusually high octane ratings and it can produce aviation gasoline directly from the original charging stock. By changing the oil feed and the catalyst, a Houdry unit may be adapted to the production of other gasolines or toluene.

All fixed-bed catalytic processes are variations of the Houdry process, although many have their own names. Other fixed-bed catalytic process include cycloversion, developed by the Phillips Petroleum Company and in whose refinery the only plant of which is now operating. Little operating data are available on this plant, built in 1944. Hydroforming (described fully in the next section, see "Hydroforming", page 21) is another variety of the original Houdry design.

## HYDROFORMING(1, 10, 12, 20, 28, 29, 30, 35)

For many years it had been known that with the aid of certain dehydrogenation catalysts, naphthenes with a six membered ring and normal paraffins could be converted to aromatics, but processes using these catalysts had never become commercial because the catalysts became rapidly inactivated from the fouling by carbonaceous deposits. Houdry eliminated this drawback to some extent with his catalyst cycle timing system. In the cyclization reactions, carbon deposition is especially serious.

It was found that these carbonaceous deposits can be minimised if the reaction is carried out in the presence of hydrogen. With suitable catalysts and under suitable conditions, the hydrogenation process can be operated for many months without carbon deposition on the catalyst and carbonaceous matter can even be converted to liquid products.(10) Such conditions, however, because of the high partial pressure of hydrogen that must be maintained, fail to give the degree of conversion to aromatic hydrocarbons considered necessary for commercial success. Therefore, a modification of the hydrogenation process was devised to obtain the benefit of the hydrogen atmosphere without, however, consuming hydrogen, thus making it unnecessary to supply hydrogen to the process. By recirculating hydrogen-rich product gas to the catalyst chambers and operating at a moderate pressure on select-

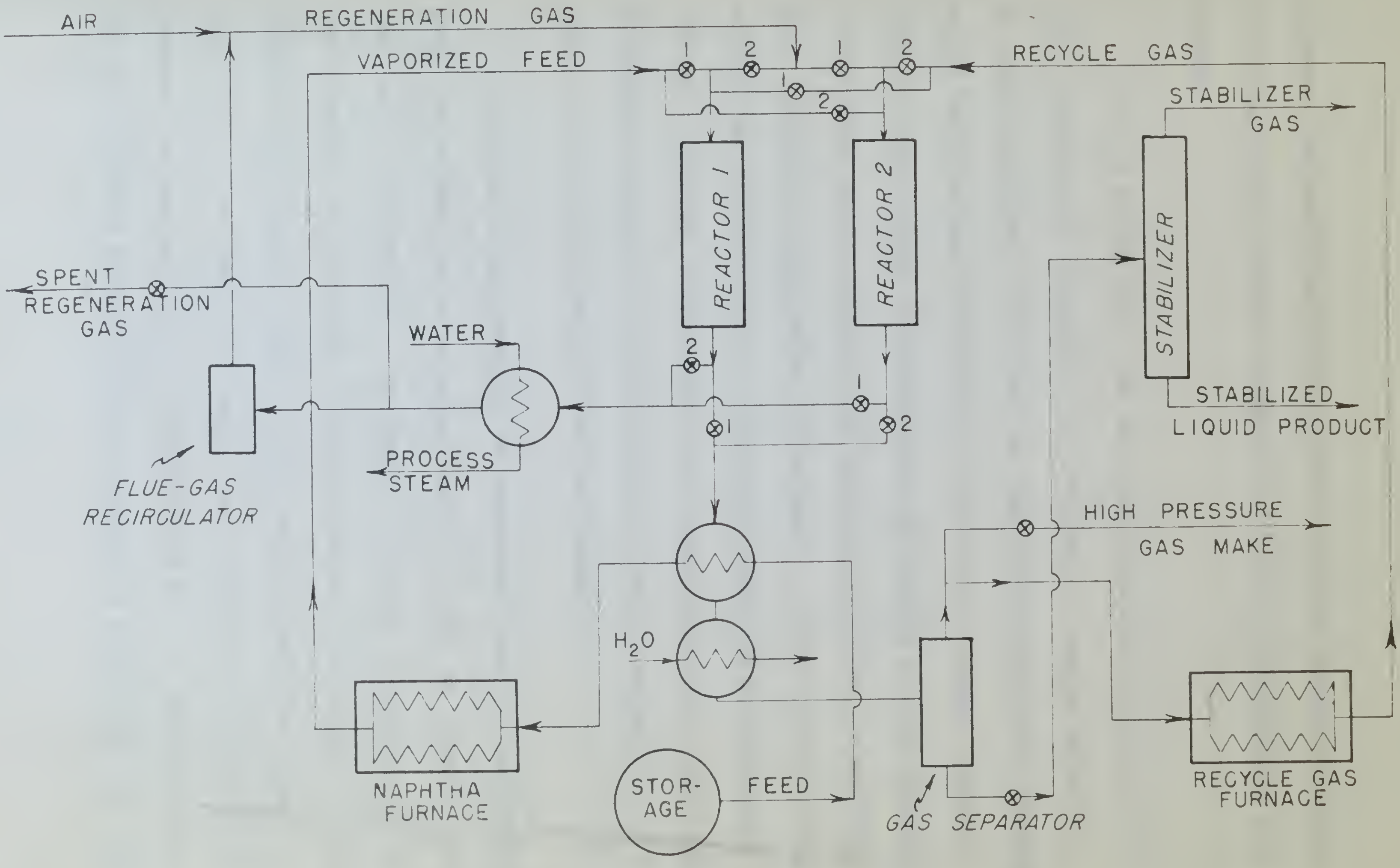
ed feed stocks, the formation of coke on the catalyst is greatly reduced and the catalyst remains active for a relatively long period of time. This modification is called hydroforming, or catalytic reforming, since molecules are reformed into aromatics in the process. This process is used today in most of the plants producing synthetic toluene.

Hydroforming was actually developed, as mentioned above, for the desulfurization and octane improvement of low-quality naphthas. Hydroforming grew out of the cooperative reserach carried out by the M. W. Kellogg Company in the mid thirties with four major oil companies. Process design was worked out by Kellogg and Standard Oil of Indiana. The first commercial unit was set in operation in 1940 by Pan American Refining Corporation at its Texas City refinery. When the toluene extraction process was worked out, largely by Standard Oil of New Jersey and Shell Oil Company, hydroforming became of great interest as a source of nitration-grade toluene. There were, in July of 1945, eight hydroforming units in operation. The Baytown Ordnance Works operated by the Humble Oil and Refining Company and costing twelve million dollars was the first commercial plant for the production of synthetic nitration-grade toluene from petroleum. A hydroforming by-product containing xylenes and other aromatics constitutes an important source of scarce rich-mixture ingredients. The post-war survival

of hydroforming depends on the increase in the life of the catalyst and a decrease in the cost of maintenance. Both of these improvements seem likely.

Figure 2, page 24, illustrates the following discussion of the hydroforming plant itself. Figure 2 shows a flow sheet for a typical hydroforming plant. The principal reaction in the process is the dehydrogenation of methyl cyclohexane (MCH) with heat and in the presence of hydrogen and a catalyst to give toluene and free hydrogen. Fresh feed is heated to reaction temperature, first by means of a heat exchanger where it receives heat from the products of the reactor, and then by means of a so-called naphtha furnace. At the entrance to the reactor, the hot oil vapor is joined by hot recycle gases which may contain between forty and eighty per cent by volume of hydrogen, depending on the feed stock and the catalyst conditions used. The joined streams of oil vapor and recycle gases pass through one of the two reactors where the catalyst is disposed and where conversion takes place. The product is cooled and condensed and the gas is separated from the liquid. Some of the gas is recirculated while the remainder is released as necessary to maintain the desired pressure on the system. The recycled gas is preheated before joining the stream of oil vapor in the recycle gas furnace. The liquid product is stabilized by removing the dissolved propane and lighter hydroc

FIGURE 2



HYDROFORMING PLANT

carbons. The stabilized liquid product is then treated by recovery methods (see "Toluene Recovery", page 47) to concentrate the toluene.

In spite of the fact that the coke formation is small, it is still necessary to regenerate the catalyst at regular intervals. To permit continuous operation, at least two reactors are provided; one is being regenerated while the other is on stream. Regeneration of the catalyst is accomplished by burning off the carbonaceous deposits by air diluted with spent regeneration gas and flue gas. During the regeneration of Reactor 1, for example (see Figure 2), the valves marked "1" are kept closed and valves marked "2" are kept open. This allows the regeneration gas to flow freely through Reactor 1, but not Reactor 2, and the vapors of oil and gas to flow through Reactor 2 but not Reactor 1.

The hydroforming reaction is endothermic and the temperature drop from reactor inlet to outlet may be as much as several hundred degrees (Fahrenheit). To narrow the range of temperature in the reaction, two reactors in series with an intermediate reheating furnace may be used in place of each reactor shown in Figure 2, page 24. At the conditions used, the equilibrium relationships promote the dehydrogenation of naphthenes and the hydrogenation of any aliphatic olefins that may already be present in the feed

or that may tend to form. The latter reaction accounts largely for the lower rate of coke formation in hydroforming as compared to operation without the hydrogen atmosphere. Olefins, which tend to polymerize to form coke and tar, cannot be present in high concentration on the surface of the catalyst.

Dehydrogenation of naphthenes, particularly of those with six carbon atoms in the ring, accounts for most of the aromatic production, although, some toluene is produced from other components of the feed. Data on the hydroforming of relatively pure methyl cyclohexane are given in Table II, page 27. The loss of methyl cyclohexane amounted to over ninety-seven per cent by volume of that in the feed; ninety-three per cent went into the production of aromatics. In the process, some side reactions take place which result in the production of benzene and some higher aromatics other than toluene itself. About eighty-five per cent of the methyl cyclohexane was converted to toluene. Table II shows, however, that the volumetric yield was only seventy-one per cent. This arises from the facts that hydrogen is lost in the conversion and that toluene has a higher liquid density than methyl cyclohexane. The theoretical volumetric yield from methyl cyclohexane is eighty-three per cent. In these calculations it was assumed that the two and one-half per cent of toluene in the feed passed through the operation unchanged. Data on normal heptane are also

given in Table II. Normal heptane yielded, under the conditions employed, only a relatively small amount of toluene, and, as in-

TABLE II(10)

Hydroforming "Pure" Compounds.

| Boiling point, °F → | MCH<br>214° |  | n-Heptane<br>209° |  | Toluene<br>231° |  |
|---|---|---|---|---|---|---|
|  | Feed | Prod | Feed | Prod | Feed | Prod |
| Yields based on feed, volume per cent: |  |  |  |  |  |  |
| Dry gas | --- | 9.2** | -- | 26.5** | --- | 0.9** |
| Liquid paraffins | 0.0 | 1.4 | -- | 39.0 | 0.0 |  |
| n-Heptane | 0.0 | --- | 100 | 21.0 | 0.0 | 1.2 |
| MCH | 97.5 | 2.7 | -- | 00.0 | 2.5 |  |
| Benzene | 0.0 | 4.0 | -- | * | 0.0 | 0.0 |
| Toluene | 2.5 | 71.2 | 00 | 11.7 | 97.5 | 97.9 |
| Xylenes, Ethyl benzene, and heavier aromatics | --- | 1.6 | -- | * | 0.0 | * |
| Boiling range of liquid product, °F: |  |  |  |  |  |  |
| 10 % at | 224 |  | 127 |  | 231 |  |
| 50 % at | 231 |  | 196 |  | 231 |  |
| 90 % at | 233 |  | 234 |  | 232 |  |
| Calculated conversions to aromatics, per cent: |  |  |  |  |  |  |
| MCH to total aromatics | 93 |  | -- |  | -- |  |
| MCH to toluene | 85 |  | -- |  | -- |  |
| n-Heptane to toluene | -- |  | 16 |  | -- |  |

*Not determined, but believed to be less than one per cent.
**Weight per cent

dicated by the gas yield and the boiling point range of the product, was extensively cracked to lighter hydrocarbons. Although seventy-nine per cent of the normal heptane disappeared in the reaction, only sixteen per cent was converted to toluene. The superiority of methyl cyclohexane as the feed is obvious. While

other catalysts are satisfactory for the laboratory conversion of normal heptane to toluene(3, 7, 8, 9, 17, 18, 19) (see "Catalysts", page 54) with higher yields, no commercial process has come to light.

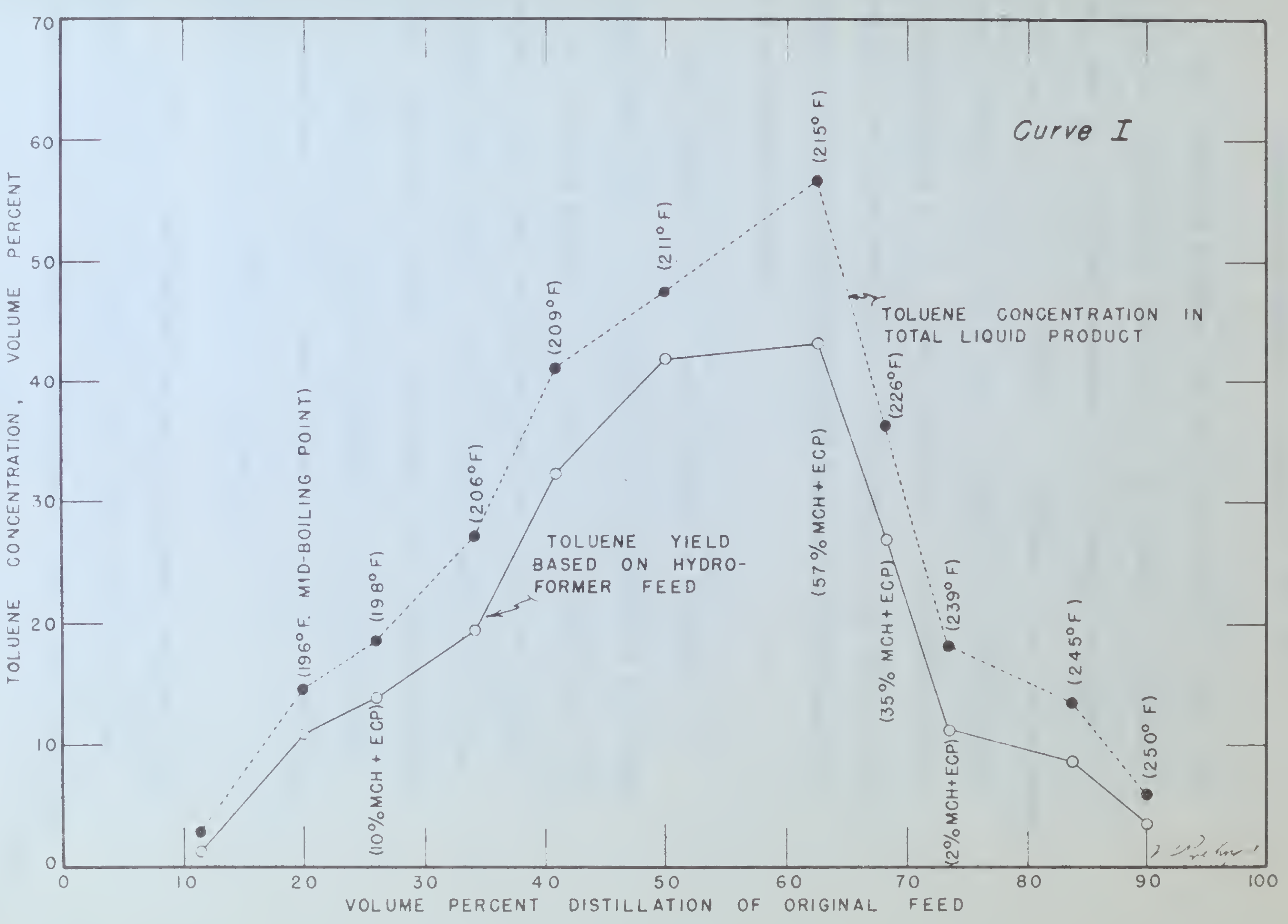
Toluene was also hydroformed to demonstrate its stability (see Table II, page 27). Little, if any, conversion occurred and it has generally been assumed in evaluating practical charging stocks that any toluene in the feed will appear in the hydroformed product.

The boiling points of toluene and methyl cyclohexane are such that both can be conveniently included in a narrow cut of naphtha charging stock; therefore the synthetic and natural toluene appear together in the hydroformed product. Many other compounds are present in the feed. However, experience with many feed stocks has shown that the toluene yield can to a large extent be accounted for on the basis of the toluene and methyl cyclohexane content, and that, while the cumulative contribution of all other compounds present is an important consideration, the toluene yield from any one is probably quite small.(10) An exception is methyl cyclohexene which occurs in cracked stocks and appears to be converted to toluene in high yields.

It will be seen then, that the methyl cyclohexane content of potential feed stocks can be used to calculate approximately their capacities to yield synthetic toluene by the hydroforming process. The methyl cyclohexane content, together with that of toluene, is shown in Table I, page 7. This methyl cyclohexane content is always greater, and in many cases ten times as great, as the toluene content. It is obvious then, that by converting the methyl cyclohexane to toluene, much less crude need be processed and much less equipment is required to produce nitration-grade toluene than if only the natural toluene were extracted. In analyzing potential feed stocks, it was not possible to distinguish between the isomers methyl cyclohexane and ethyl cyclopentane. The boiling points of these isomers differ by only 3° F and their general physical properties are nearly the same. Therefore, the values given in the second column of Table I, page 7, include such ethyl cyclopentane as is present. Indications are that the methyl cyclohexane - ethyl cyclopentane mixture may contain about fifteen to twenty per cent of ethyl cyclopentane. By comparison with di-methyl cyclopentane, which has been shown to yield only a limited amount of toluene, it is to be expected that the ethyl cyclopentane would produce much less toluene than the methyl cyclohexane, and it is necessary to take this into account when evaluating various feeds on the basis of their methyl cyclo-

hexane - ethyl cyclopentane content.

To determine the extent to which the toluene producing component of the feed could be concentrated in a narrow boiling fraction, a typical 200° to 250° F virgin naphtha was fractionated into narrow cuts at a nine-to-one reflux ratio in a twenty-four plate column, and several of the cuts were subjected to hydroforming. The highest yield was forty-four volume per cent (see Curve I, page 31). In this case the feed contained fifty-seven per cent methyl cyclohexane plus ethyl cyclopentane and five per cent toluene. The toluene concentration in the product was fifty-nine per cent; on a broader feed it would be considerably lower.


Curve I
TOLUENE CONCENTRATION IN TOTAL LIQUID PRODUCT
TOLUENE YIELD BASED ON HYDROFORMER FEED
(196°F. MID-BOILING POINT)
(198°F)
(206°F)
(209°F)
(211°F)
(215°F)
(226°F)
(239°F)
(245°F)
(250°F)
(10% MCH + ECP)
(57% MCH + ECP)
(35% MCH + ECP)
(2% MCH + ECP)
TOLUENE CONCENTRATION, VOLUME PERCENT
0
10
20
30
40
50
60
70
VOLUME PERCENT DISTILLATION OF ORIGINAL FEED
0
10
20
30
40
50
60
70
80
90
100

# THERMOFOR CATALYTIC CRACKING[1, 27, 33]

The thermofor process was the first attempt to get away from the intermittent operation in the Houdry, the hydroforming, and all fixed-bed processes, for although the plant as a whole was operated on a simulated continuous flow, the catalyst cases themselves were shut down to permit the revivification or regeneration of the spent catalysts. As is evident from studying the fixed-bed types of processes, a far greater case volume is required for the process than is actually used at any one time on stream.

The thermofor process was developed to eliminate the intermittent flow in the catalyst cases themselves and makes use of a moving catalyst bed instead of the fixed-bed. The method in which this moving catalyst bed could be utilized presented many problems, but was finally worked out by the Socony Vacuum Oil Company. In essence, the process consists of a moving-bed of catalyst, conducted on its way by means of mechanical conveyors through first the reactor, and then a kiln in which the catalyst is regenerated.

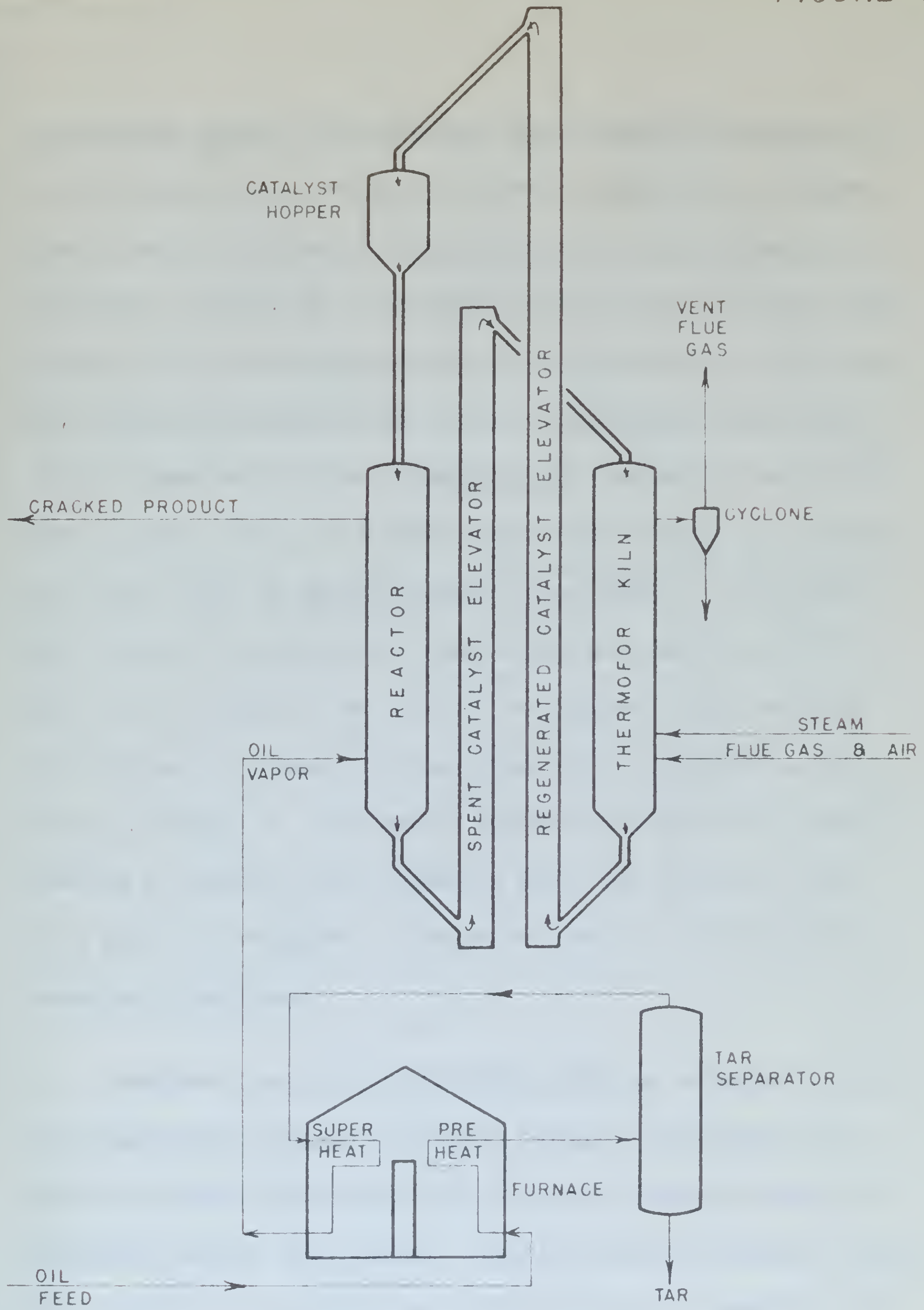
In 1941 a five-hundred-barrel pilot-plant unit was set in operation at the Paulsboro, New Jersey refinery of the Socony Vacuum Oil Company. In October of 1943, the first full-

scale commercial thermofor plant was operated at the Beaumont, Texas, refinery of the Magnolia Petroleum Company. In June of 1945 there were thirty-four thermofor reactors in operation throughout the country, with a total nominal charging capacity of 324,000 barrels daily, representing about thirty-one per cent of the three major catalytic processes, Houdry, fluid and TCC. Some TCC units have produced as high as seventy per cent over the rated capacity.

Figure 3, page 34, gives the flow sheet showing the important elements of the TCC process. The TCC process involves passing charging stock vapors through a moving (solid bed) mass of catalyst particles or of passing liquid charging stock or a mixture of liquid and vapor down through the moving bed. The vapors are usually passed upward. The oil feed is first rid of the tar by flashing in a tar separator, as in the Houdry plant (page 14), and is then passed through a superheater and into the reactor, where it flows up against the downflowing catalyst. At the top of the reactor the cracked product is withdrawn and sent to whatever unit is used for recovery of the toluene (see "Toluene Recovery", page 47).

The distinguishing feature of the TCC process is the flow of the catalyst and the method for rendering the process con-

FIGURE 3



THERMOFOR CATALYTIC CRACKING UNIT

pletely continuous. The catalyst is a treated clay instead of the bead catalyst used in fixed-bed processes. It moves down through the reactor by gravity and enters a diagonal lead from the base of the reactor to the spent catalyst elevator. In the spent catalyst elevator the catalyst is lifted by a bucket conveyor to the top of the elevator tower where it is dumped into another diagonal leg leading to the top of the thermofor kiln. The mass moves down through the thermofor kiln, again by gravitational force, against the upflowing stream of regenerating gases which are composed of flue gas, air and steam. The heat of the regeneration reaction is utilized to produce process steam in a boiler unit, not shown in Figure 3. The outlet regeneration gases are sent through a cyclonic dust separator where any catalyst dust that might be entrained is separated and fed back into the catalyst flow line.

From the base of the thermofor kiln the catalyst reaches the regenerated catalyst elevator through a diagonal lead. From the top of the regenerated catalyst elevator tower the catalyst reaches the catalyst hopper by another diagonal leg. The catalyst is taken to the reactor through a vertical pipe known as the "clay leg". Considerable speculation was prevalent concerning the possibility of blowing out the clay

leg when high pressure reactor conditions were used, but tests under pressures up to the limit of the vessels tested showed that the flow of catalyst down through the clay leg was never seriously impaired. Another point is the effective seal used at the base of the reactor. The catalyst is purged with steam as it leaves the reactor, and thus is rid of all feed vapors which, in effect, are thereby sealed.

A typical plant using the thermofor process uses a reactor tower filled with baffles to effect the proper mixing of the vapors and catalyst. The tower is thirty feet high and eleven and one-half feet in diameter. The regenerated catalyst elevator is about one hundred feet high, while the spent catalyst elevator is about seventy-five feet high. The reaction temperature used is about 800° F to 1000° F, as in the processes previously discussed. The pressure is between ten and fifteen pounds per square inch gauge. The space velocity may be varied between 0.2 and 3.0 cubic feet of vapor per cubic foot of catalyst per hour. The catalyst residence time in the reaction zone may be varied from a few minutes to two hours, depending on other operating conditions and the catalyst used.

Interesting among recent improvements in the original process is the use of steps in the diagonal feed legs through which the catalyst flows. Serious erosion problems were presented by the flow of hot clay catalyst down the diagonal legs, and these legs had to be replaced more often than was expected. To eliminate this wear, steps were installed in the diagonal so that the clay catalyst was forced to flow or cascade over the steps. Thus the catalyst built up a layer on the steps and instead of flowing against the legs, it flowed over itself and reduced the erosion to a minimum.

The thermofor catalystic cracking process differs from the Houdry process only in that it effects a continuous operation through the use of a moving bed of catalyst. The catalyst must still be regenerated as before, but the efficiency of operation is greatly improved.

## THE FLUID CATALYST PROCESS(1, 25)

The fluid catalyst process represents a new chemical engineering technique which has wide application to industrial operations, both catalytic and non-catalytic. This principle may soon be applied to such operations as ore reduction, coking of coal, water gas manufacture and other specialized chemical processes, regardless of their respective operating pressures. This development has been successfully applied to the catalytic cracking of petroleum fractions.

The fluid process operates on the principle of a moving bed of catalyst, as does the TCC process, but the fluid process does not handle the catalyst mechanically at any stage of the process.

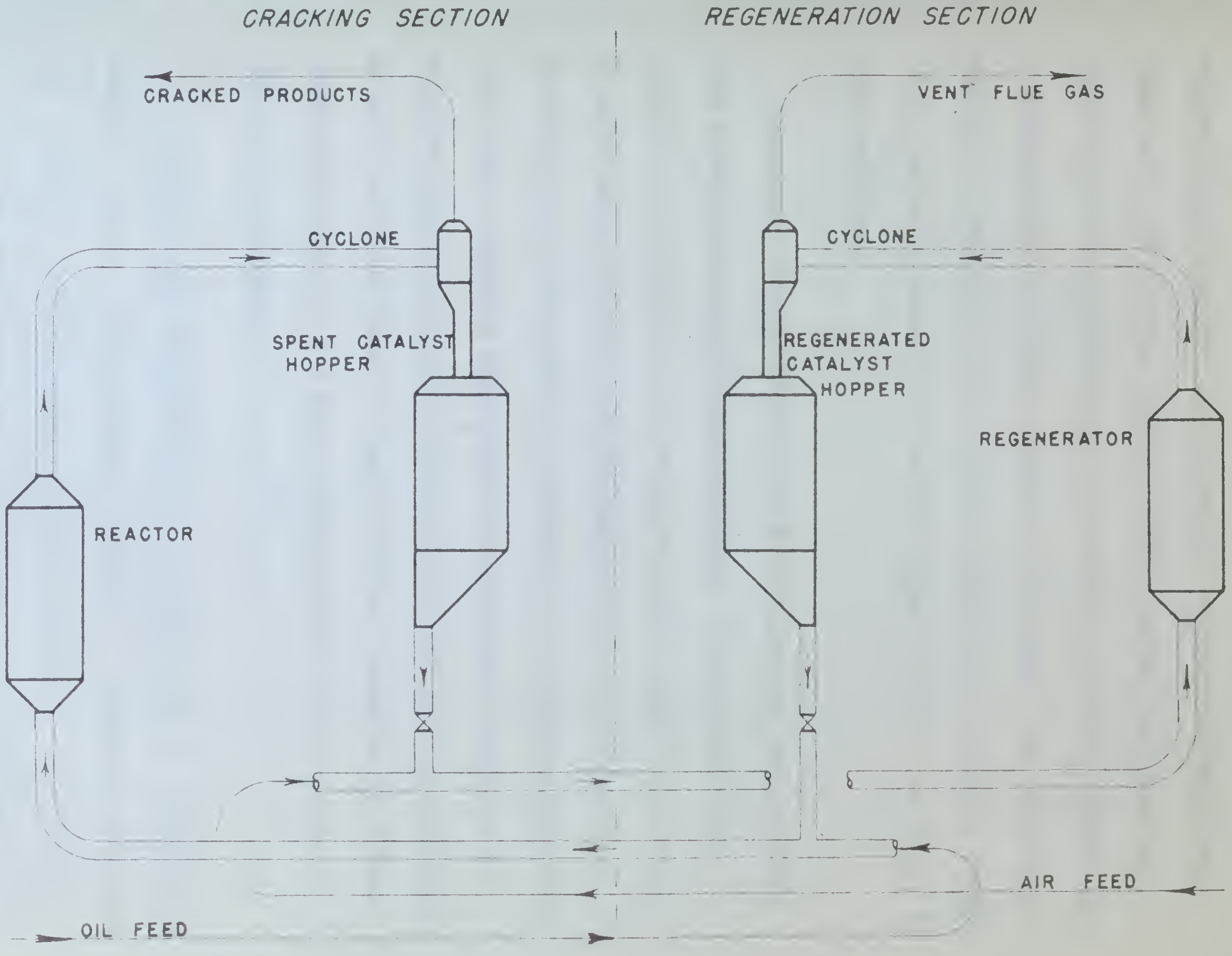
The first fluid catalyst plant was placed on stream at the Baton Rouge, Louisiana, refinery of the Standard Oil of New Jersey Company in 1942. By June of 1945, there were thirty-two plants operating on the fluid catalyst process in the United States, with a nominal throughput of 400,000 barrels daily. Four are of the upflow type; the rest utilize the more recent downflow method. The world's largest fluid catalyst cracking plant was placed on stream in December of 1944 at the Avon refinery of the Tide Water Associated Oil

Company.

The fluid catalyst process, as stated above, employes a new technique in handling solid materials. The solid material, in a powder form, is kept in a fluid or freely flowing condition at all times, and can thus be handled in much the same way as a liquid. A fluidized mass can be circulated by application of the gas-lift principle — that is, by balancing a downflowing stream of high-solids density against an upflowing stream of low-solids density. In other words, the required pressure differential for circulation is obtained in much the same way as water would be transferred by balancing a column of water against a water-gas mixture.

The basic equipment involved is illustrated in Figure 4, page 40. There are two primary zones, a cracking and a regeneration zone. The principal apparatus is the same in each zone: standpipe, reaction vessel and dust separator. Oil vapor is contacted with regenerated catalyst delivered by gravity from a standpipe, and the mixture flows in suspension into the cracking reactor where the reaction occurs. The mixture of cracked petroleum and catalyst flows through cyclonic dust recovery equipment where the catalyst is recovered. The separated spent catalyst is collected in a hopper, flows

FIGURE 4



CATALYST FLOW IN FLUID CRACKING PROCESS

at high density down a standpipe, and is injected into the stream of air used for regeneration. This air carries the spent catalyst to other regeneration vessels, and from there into another set of cyclonic dust collectors where almost all of the catalyst is removed from the flue gas. The recovered catalyst is collected in a hopper, flows down through a standpipe, and is injected into the oil vapor stream. The cycle is thus completed.

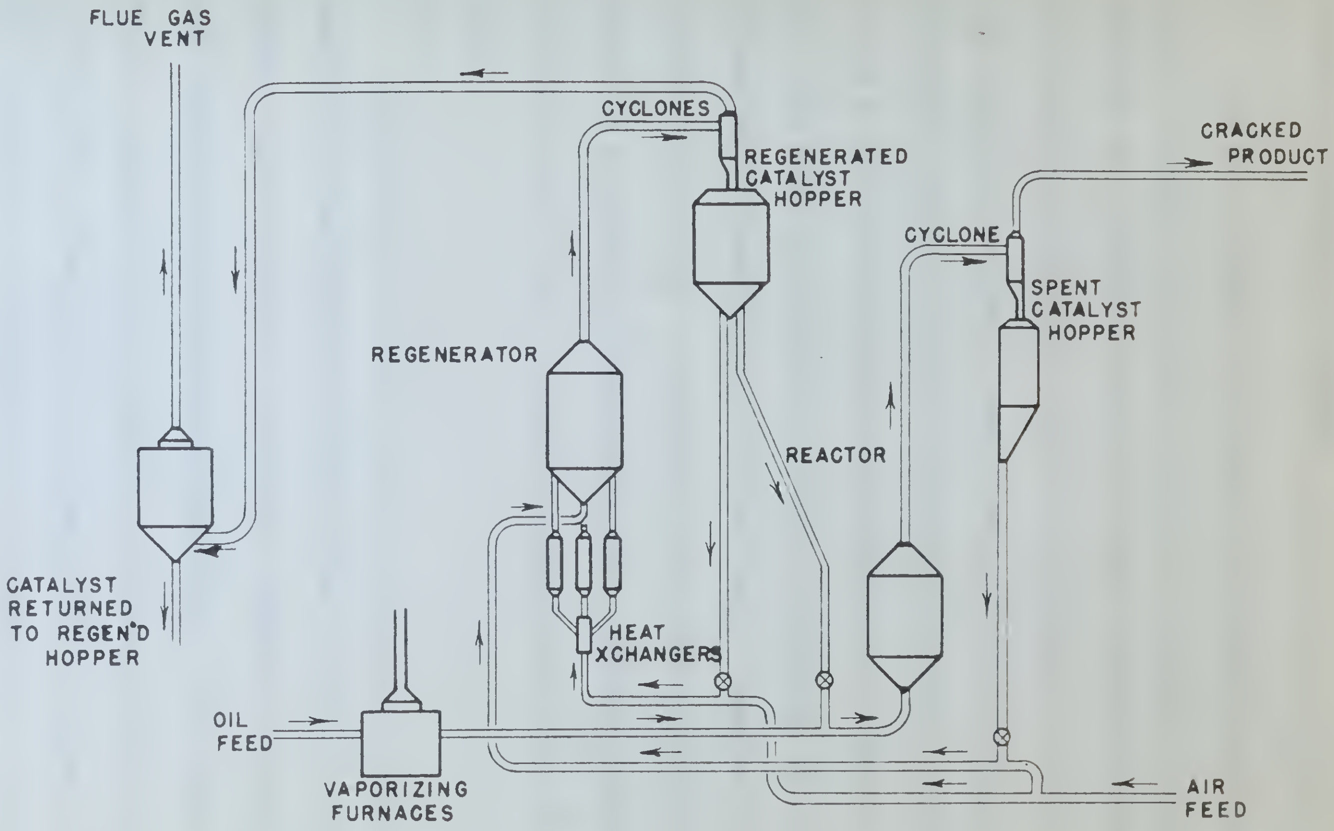
The flow characteristics of gases carrying solid particles have been carefully investigated. It has been found possible, by suitable adjustment of gas or vapor velocities, to build up relatively high concentrations of solids where desirable, as, for example, in reaction and regeneration vessels. The densities that can be obtained are functions of the feed rate, composition and particle size of the particles, as well as of the vapor or gas velocity. Pressure drop from friction is small; the main pressure drop in the system is due to static heads.

Although high concentrations of solids may be obtained in reaction vessels, the solid-gas mixture is extremely turbulent and resemble a boiling liquid in many respects. As a result of this high turbulence, with consequent rapid circulation of

solids, the temperature throughout the solids mass is surprisingly uniform, varying less than five degrees fahrenheit from bottom to top in large vessels in catalytic cracking. The extreme turbulence of the solids in vessels of this type offers many advantages in temperature control in catalytic or other processes.

Figure 5, page 43, shows the flow sheet of a typical fluid catalyst cracking plant. Regenerated catalyst from a storage hopper flows by gravity through a standpipe and is injected into the fresh oil feed vapor which carries it to the cracking reactor. The velocity in the reactor is low, to maintain a high concentration of catalyst, and cracking occurs with the subsequent deposition of carbonaceous materials on the catalyst. The mixture of cracked products and spent catalyst from the cracking zone is separated in cyclonic dust recovery equipment; the cracked products flow to recovery equipment (see "Toluene Recovery", page 47) for separation into desired components. The spent catalyst drops into a storage hopper, flows down a standpipe, is picked up by an undulating air stream and is carried to the regenerator in which the carbonaceous deposits are removed by combustion. The mixture of flue gas and catalyst from the regenerator are separated, the catalyst dropping into the regenerated catalyst

FIGURE 5



FLUID CATALYST CRACKING PLANT

hopper to complete its cycle.

The heat evolved in burning the carbonaceous deposits on the catalyst is greater than can be absorbed as sensible heat by the catalyst without excessive temperature rise. It is therefore necessary to have an additional means of absorbing regeneration heat. This is done by circulating the regenerated catalyst through shell-and-tube heat exchangers, using a separate standpipe circuit as shown in Figure 5, page 43. The cooling medium in the heat exchangers in the unit described is fresh oil feed to the plant. However, the heat absorbed by the oil is ordinarily more than that required to bring it to proper temperatures, and a further dissipation of this heat is made to produce process steam for use in the plant.

Operation of the fluid cracking plant is entirely automatic.(26) The ratio of catalyst flow to oil flow, for example, is controlled by a mechanism actuated by changes in the density of the catalyst-oil mixture. Flow of the catalyst to the regenerator is assured by automatic control of the level of the catalyst in the spent catalyst hopper. Similarly, the regenerator temperature is governed by the automatic regulation of the quantity of catalyst circulated through the heat exchangers.

The flexibility of the fluid process is demonstrated by the fact that operation can be carried out over a wide range of cracking and regeneration temperatures, as well as of depth of cracking bed. Reaction temperatures can be controlled by varying the amount of heat applied to the oil in the furnaces and to the hot catalyst circulated. Normal reactor temperatures lie in the range 800° to 1000° F, as in the Houdry process. The regenerator temperatures can be varied over a relatively wide range, but are normally kept between 1000° and 1200° F. The depth of cracking is governed by both the amount of the catalyst in the reaction zone and the ratio of catalyst to oil flow. This flexibility is important in that the character of the products is considerably affected by both the temperature and the conversion level employed.

The pressure level can also be held at any desired point within the safe range for the vessels used. In most present installations for gas-oil cracking, the pressure at the top of the reactor vessel is about ten pounds per square inch gauge; that at the top of the regeneration vessel is about atmospheric.

Cracking with a suitable catalyst (see "Catalysts", page 54) at elevated temperatures produces, in addition to high yields of olefins and isobutane for alkylation, a gasoline fraction containing fairly large amounts of toluene, xylenes and the higher aromatics.

## TOLUENE RECOVERY(1, 4, 11, 20, 23, 31)

As can be seen, an aromatic-rich mixture can be obtained by several means. The success of a commercial operation for manufacturing synthetic nitration-grade toluene does not rest solely on the development of a practical method for producing the toluene in quantity from petroleum, but also requires a satisfactory solution of the problem of separating the toluene from the other components boiling in the same range, to produce the high degree of purity demanded by nitration-grade specifications. Separation by superfractionation alone, even under most favorable conditions and with a great many equivalent plates was not satisfactory, because of the very small differences between the boiling points of the impurities and that of toluene itself. Moreover, toluene forms azeotropic mixtures with some of the other components of the cracked stock; these mixtures boil at temperatures different from that of pure toluene, and cannot be resolved by simple distillation methods.(20)

Processes for the liquid-phase solvent extraction of aromatics from hydrocarbon mixtures were known, but the highest aromatic concentration obtainable by the known methods was only about seventy-five to eighty percent, while the

specifications for nitration-grade toluene called for above 99 per cent purity. This problem had not arisen in making toluene from coal tar because that product contains little naphthenic, paraffinic or olefinic material, and toluene can be separated readily from the other aromatics by chemical purification and simple distillation.

The method used by practically all of the recovery plants in use today is that of azeotropic distillation. An azeotropic mixture is one which forms a constant-boiling mixture which boils at a temperature different from, and usually lower than the boiling point of either of the constituents. Azeotropes may be formed between two, three, or more components.

Azeotropic mixtures by which toluene may be separated are those in which the impurities form an azeotrope with the azeotrope-former added before distillation, and in which the azeotrope boils in a range far enough removed from that of pure toluene to permit the mixture to be fractionated readily. Such azeotrope-formers vary widely in character. Mixtures of methanol and water,(31) methylethylketone (MEK) and water,(20) and a low molecular weight nitro paraffin (i.e. nitropropane)(4) have been suggested. By far the most

widely used azeotrope-formers today are MEK-water and methanol-water mixtures.

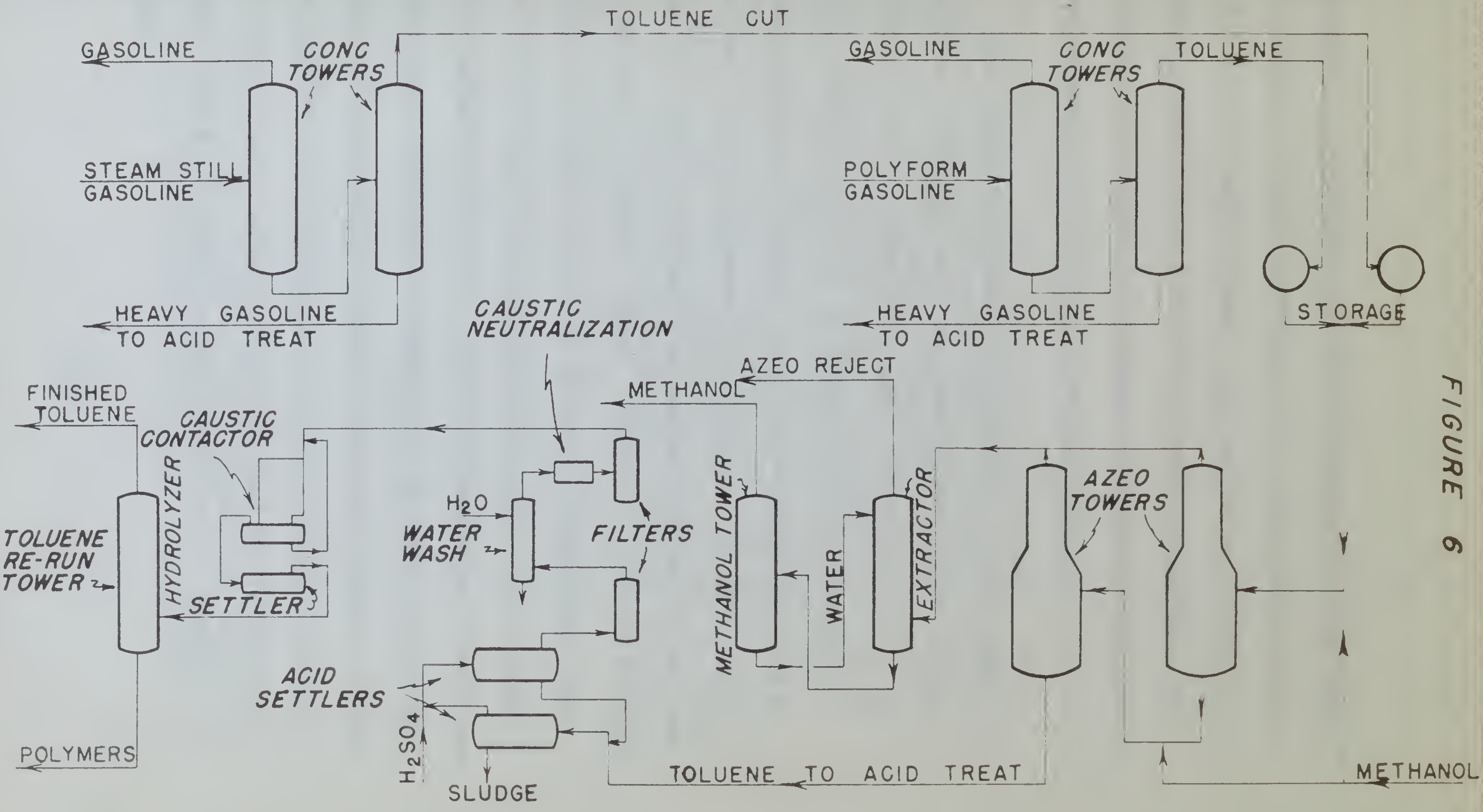
Figure 6, page 50, shows the flow sheet of the Magnolia Petroleum Company's toluene recovery plant, Beaumont, Texas. This plant uses the methanol-water mixture.

The toluene recovery consists of four main steps: the preparation of a toluene concentrate boiling in between 215° to 245° F, the concentration of the toluene cut to ninety-eight per cent toluene by azeotropic distillation with methanol and water, and the purification of the concentrated toluene obtained in the second step by an acid treatment, and the rerunning of the toluene to provide nitration-grade product.

There are two parallel systems for the concentration of the initial toluene cut. Each receives cracked vapors from steam-still gasoline plants and a polyforming gasoline plant. This feed might be from any of the catalytic cracking processes already discussed.

Each concentration still unit consists of two fractionation towers. The top product from the first is gasoline, and is sent back to the gasoline section of the refinery for

FIGURE 6



TOLUENE RECOVERY PLANT

blending. The bottoms are sent to the second tower, where the overhead fraction consists of the concentrated toluene cut. This may carry between eight and fifty per cent of toluene, depending on the feed and other conditions. The bottoms of the second tower consist of heavy gasoline, and are returned to the refinery for acid treatment.

The toluene from each concentrator is stored prior to addition of methanol and subsequent fractionation of the azeotrope in the azeotrope towers. The overhead from the first azeotrope tower is of almost constant composition, containing about fifty-five per cent of water solution of methanol with some hydrocarbon impurity. The bottoms contain from fifty to seventy per cent of toluene and are sent to the second azeotrope tower. Additional methanol is added before the mixture enters the tower. The distillate from the second tower contains about seventy per cent methanol, and includes the remaining traces of impurities. The bottoms carry from ninety-six to ninety-eight per cent of pure toluene. The top products from the two towers join and are sent to the extractor and methanol towers for solvent recovery. The azeo rejects, shown in Figure 6, page 50, is substantially alcohol-free gasoline and is sent to the blending plant.

The bottoms from the last azeotrope tower, containing ninety-eight per cent of toluene, pass to the acid treaters where the toluene is treated with ninety-eight per cent sulfuric acid in the acid settlers. The Duriron settlers act as counter-current sludge settlers. The toluene then passes through a gravel-packed coagulator, or filter, and thence to a water wash in a tower packed with Raschig rings. After washing, the mixture is neutralized in another gravel-packed coagulator. This sequence of coagulation and water wash is used to prevent the formation of an emulsion in the neutralization step. Hydrolysis of the sulfates and sulfonates present occurs in the caustic contactor; the contact time is about one hour. The hydrolysis eliminates the breakdown of these components in the rerun tower, with the accompanying acid corrosion.

The toluene rerun tower delivers toluene with the following characteristics:(11) paraffin content, one-half of one per cent, distillation boiling point range between 110.4° and 110.8° C, specific gravity, 0.869, and a cloud point below - 20° C.

The methanol is recovered in a counter-current extraction in a tower packed with Raschig rings. The top product,

as mentioned above, is substantially alcohol-free gasoline. The bottoms, carrying thirty-one per cent of methanol, are sent to the methanol tower, which is a twenty-plate fractionation column. The recovered methanol is recycled in the process.

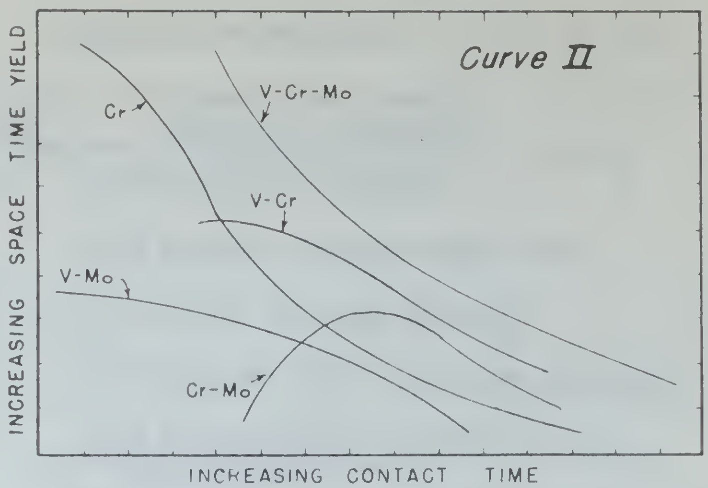
In this plant, eighty per cent of the toluene present in the feed stock is recovered. The chief losses are in the azeotrope reject and in the acid treatment and rerun steps. This method of azeotropic distillation lends itself easily to the recovery of toluene from petroleum fractions which contain a high percentage of aromatics, including toluene.

## CATALYSTS(3, 7, 8, 9, 17, 18, 19)

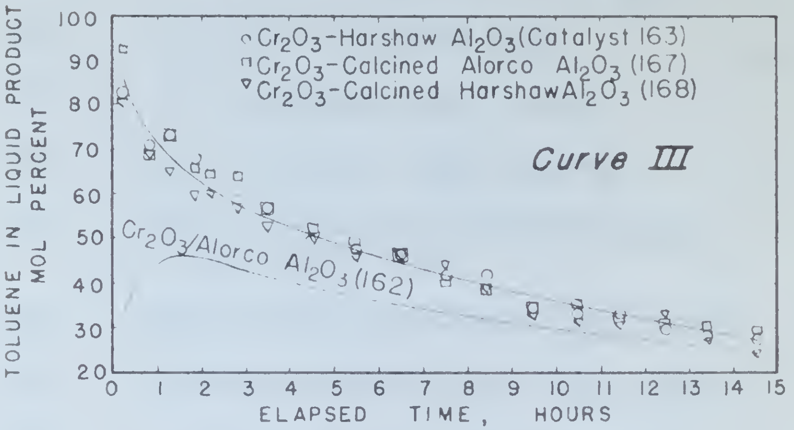
Catalysts for petroleum refining have been developed for many conditions of use. For instance, there are hydrogenating catalysts as well as dehydrogenating ones, cyclization catalysts and catalysts to break down a ring structure. Most catalysts are developed for a specific reaction. The petroleum catalysts consist of a large variety of clays. These catalysts usually contain metallic compounds formed with metals of the fourth, fifth and sixth groups of the periodic chart of elements. These compounds (largely oxides) are suspended on what is known as a carrier or supporter, which consists of activated silica or alumina. This whole mixture is formed into beads, pellets, granules, clay or dust according to the type of process in which it is to be used. The method of preparation of these catalysts is very important, since excessive temperatures can ruin them for some reactions. Various trace elements, known as promoters, may be added. These help to segregate the reaction for which the catalyst is designed from others for which the parent oxide may be active.

Grosse, Morrell and Mattox(19), of the Universal Oil Products Company, are responsible for the illustration in Curve II, page 56. This curve illustrates the effect of the nature of the different metals used as the catalyst on the activity of the catalyst for dehydrogenating and cyclising normal heptane to produce toluene. Greater activities of catalysts and larger space-time yields may be obtained with mixed catalysts containing two, three, or even more dehydrogenating metal oxides. Curve II illustrates the results of specific dehydrocyclization of normal heptane at 500° C by various mixtures of chromium, vanadium and molybdenum. The vanadium-molybdenum catalyst is always lower in activity than is the simple chromium catalyst. The mixture of all three proved to be the best, as might be expected, although the results were not additive on a simple scale.

Archibald and Greensfelder,(3) of the Shell Development Company, are responsible for the remaining curves. Table III, page 57, is a compilation of data given in their article(3) and serves to identify the various catalyst numbers and the compositions of these catalysts. Chromium oxide-alumina catalysts are prepared by one of two methods;



*Dehydrocyclization of n-Heptane into Toluene with Metal Oxide Catalysts*



*Effect of Calcining Alumina for 6 Hours (700° C) on Cyclization Activity of Catalysts (n-Heptane as Feed)*

## TABLE III(3)

### Catalyst Compositions

| Catalyst Number | Composition (Weight percent of elements) |
|---|---|
| 120 | 13.7 Cr/alpha $Al_2O_3 \cdot H_2O$ |
| 44 | 0.59 Ce/10.6 Cr/alpha $Al_2O_3 \cdot H_2O$ |
| 61 | 1.0 K/10.6 Cr/alpha $Al_2O_3 \cdot H_2O$ |
| 111 | 0.78 Ce/1.56 K/13.7 Cr/alpha $Al_2O_3 \cdot H_2O$ |
| 112 | 0.57 Ce/1.14 K/11.1 Cr/gamma $Al_2O_3$<br>($SO_4$ 0.008% of $CrO_3$) |
| 116 | 1.14 K/11.1 Cr/gamma $Al_2O_3$ |
| 132 | 0.217 Li/12.5 Cr/gamma $Al_2O_3$ |
| 139 | 0.56 Ce/1.11 K/10.6 Cr/gamma $Al_2O_3$<br>($SO_4$ 0.062% of $CrO_3$) |
| 140 | 0.57 Ce/1.14 K/10.0 Cr/gamma $Al_2O_3$<br>($SO_4$ 0.37% of $CrO_3$) |
| 150 | 0.71 Ce/1.18 K/11.3 Cr/gamma $Al_2O_3$ |
| 152 | 3.4 Ce/11.2 Cr/gamma $Al_2O_3$ |
| 162 | 12.2 Cr/Alorco $Al_2O_3$ (alpha) |
| 163 | 10.7 Cr/Harshaw $Al_2O_3$ (gamma) |
| 166 | 0.71 Ce/1.18 K/11.3 Cr/gamma $Al_2O_3$<br>($SO_4$ 5.0% of $CrO_3$) |
| 167 | 10.6 Cr/Calcined Alorco $Al_2O_3$ (gamma) |
| 168 | 11.0 Cr/Calcined Harshaw $Al_2O_3$ (gamma) |
| 171 | 0.67 Ce/1.11 K/10.6 Cr/gamma $Al_2O_3$ |

coprecipitation of the hydroxides of chromium and alumina or impregnation of alumina with a solution of chromic acid or a chromic salt. In both cases the material is subsequently calcined to remove water and volatile acids.

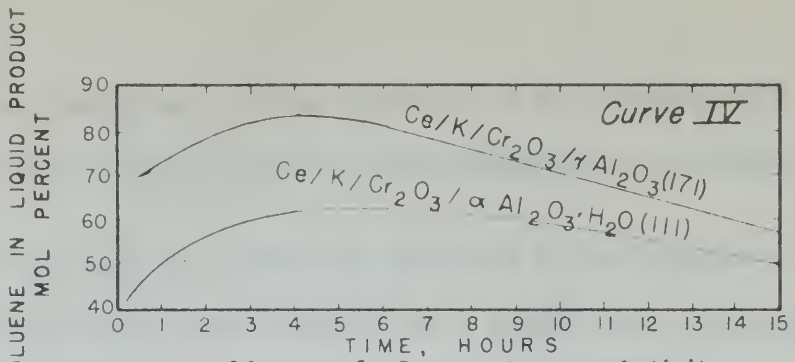
The impregnation method is simpler, and under the conditions of preparation and with the promoters to be discussed, it results in a catalyst equalling or exceeding the activity of those made by coprecipitation of chromium and aluminum oxides. The carriers used were alpha $Al_2O_3 \cdot H_2O$, or Böhmite; gamma $Al_2O_3$, the anhydrous form of Böhmite; and alpha $Al_2O_3$, or corundum, the natural or synthetic high-temperature form.

Activity tests were ordinarily made under the following conditions. In the presentation of test results, any deviation from these standards are indicated. A temperature of 450° C, atmospheric pressure, catalyst bed used was 16 inches long and five eighths of an inch in diameter with an axial thermowell, the catalyst volume was sixty-nine cubic centimeters, the liquid feed rate was twenty-five milliliters per hour and the liquid hourly space velocity (LHSV) was maintained at 0.36 volumes per volume of catalyst space per hour.

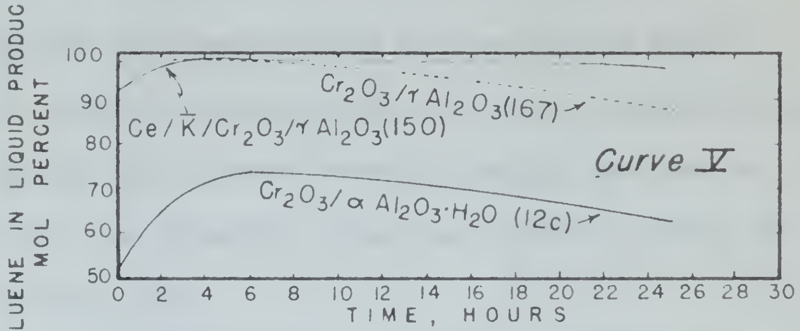
Curve III, page 56, shows the effect of calcining the alumina used as the catalyst support for six hours at 700° C on the cyclization activity of catalysts using normal heptane as the feed. The calcined or equivalent carrier is superior.

Curve IV, page 60, illustrates the effect of two types of supporters on a cerium-potassium-chromia-alumina catalyst. The two supporters, alpha and gamma $Al_2O_3$, were tested alone and showed no activity. Again, the calcined form is superior.

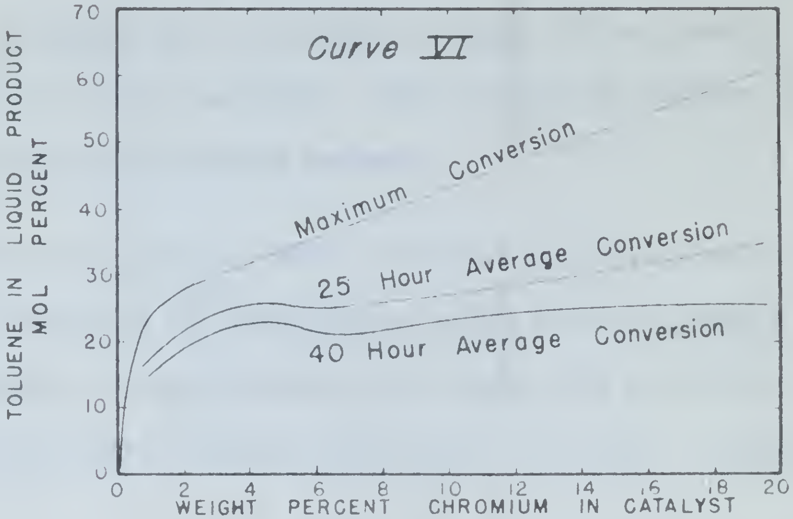
Curve V, page 60, gives a comparison of catalysts for the dehydrogenation of methyl cyclohexane. Some catalysts, notably those represented by the upper curves, were promoted, while others were not. The lower curve represents the activity curve for an unpromoted chromia-alpha alumina catalyst and indicates that this catalyst is definitely inferior to the others, a promoted catalyst and an unpromoted catalyst both of which use gamma alumina. The promoted catalyst illustrated is superior to both of the unpromoted catalysts after several hours have passed (the time in hours represents the life of the catalyst, i.e.



Effect of Supports on Activity



Comparison of Catalyst Promoters



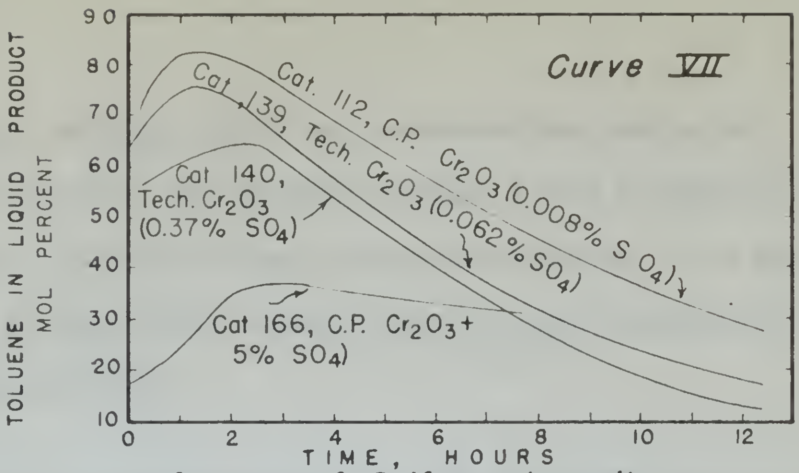
Influence of Chromium on Activity

the ordinate corresponds to the activity of the catalyst after it has been on stream for the time indicated as abscissae).

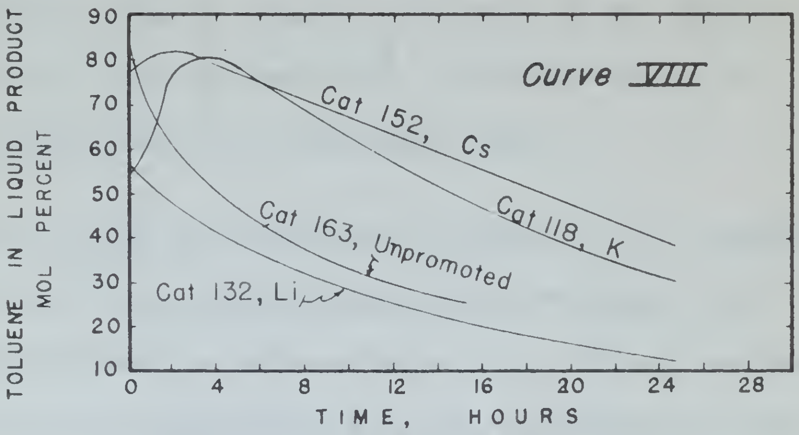
Curve VI, page 60, shows the influence of the chromium content on the cyclization activity of a $Cr_2O_3$/alpha $Al_2O_3 \cdot H_2O$ catalyst. The maximum conversion is that at which the resulting toluene yield was the greatest. A small addition of chromium increases the catalyst activity sharply, while increasing amounts of chromium added to the catalyst tend to increase the activity linearly after the first sharp increase. However, the ten and twenty-five-hour averages are more or less flat after the chromium content has reached a value of three or four per cent.

Curve VII, page 62, illustrates the effect of sulfate impurities on the catalyst activity. The sulfate ion seems to be the most deleterious of all impurities normally found in chromia. Catalyst 166 (see Table III, page 57) was made by adding sulfate to the catalyst. Small amounts of sulfate impurity decrease the activity markedly.

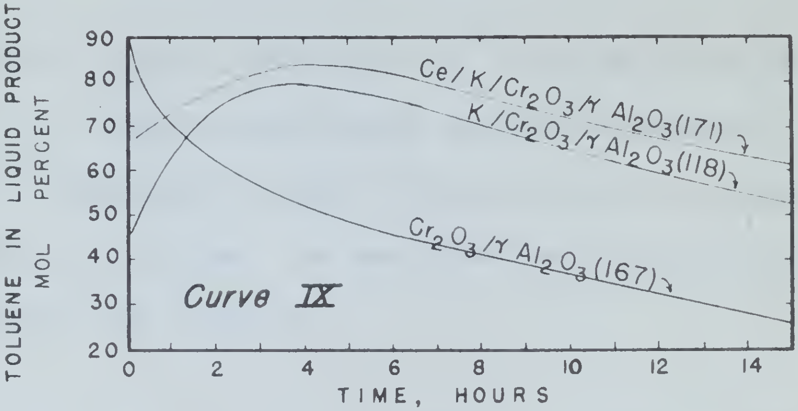
Curve VIII, page 62, shows the effect of various alkali metals as promoters on a $Cr_2O_3$/gamma $Al_2O_3$ catalyst (12½ per cent chromium on a gamma carrier with 0.028 mols of the alkali metal indicated added per 100 mols of catalyst). Lithium



Influence of Sulfate Impurity on Activity



Effect of Alkali Metals as Promoters



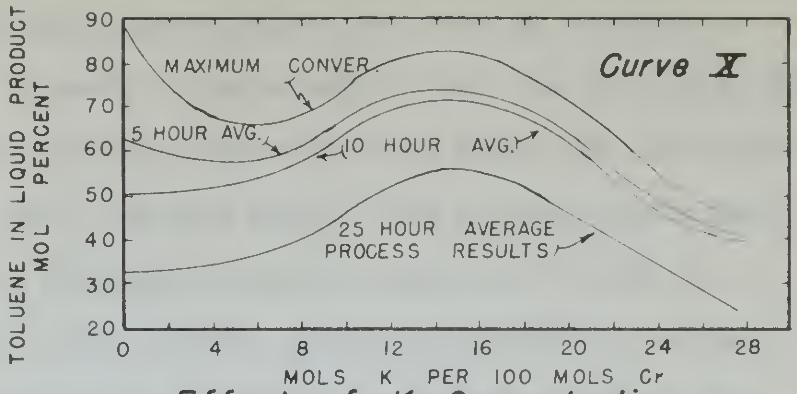
Effect of Ce and K as Promoters

reduces the activity, while both potassium and cesium increase it greatly. The promoted catalysts show a period of induction of about four hours, while the activity of the unpromoted catalyst falls steadily from the very beginning of the reaction period.

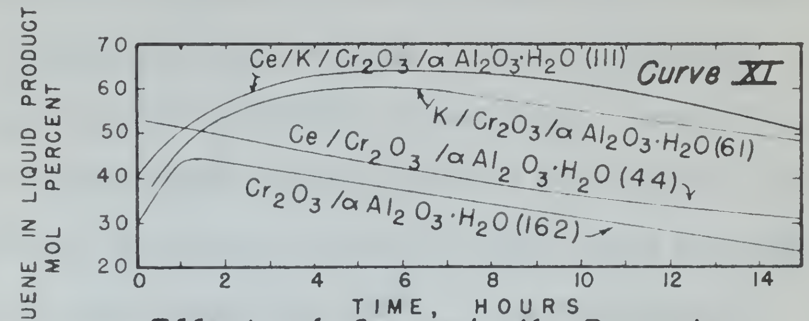
Curve IX, page 62, illustrates the same effects of cerium and potassium on the chromia-alumina catalyst as promoters. The induction period is clearly illustrated in the expanded time scale over that of Curve VIII. As stated before, the induction period lasts for about four hours.

Curve X, page 64, illustrates the effect of the potassium concentration of the chromia-gamma alumina catalysts. The "hump-backed" curve is characteristic of all average conversions. A potassium concentration of ten to eighteen mol per 100 mols of chromium gives the best activity.

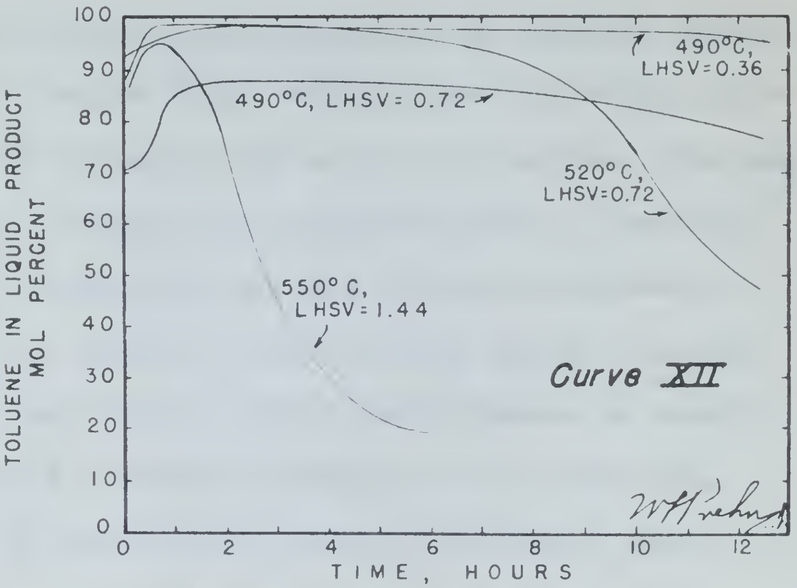
Curve XI, page 64, illustrates the effect of cerium and potassium on a chromia-alpha alumina catalyst as promoters. The effects illustrated in Curve IX, page 62, are on a gamma alumina catalyst carrier. The same deductions can be drawn that were drawn for Curve IX.



Effect of K Concentration



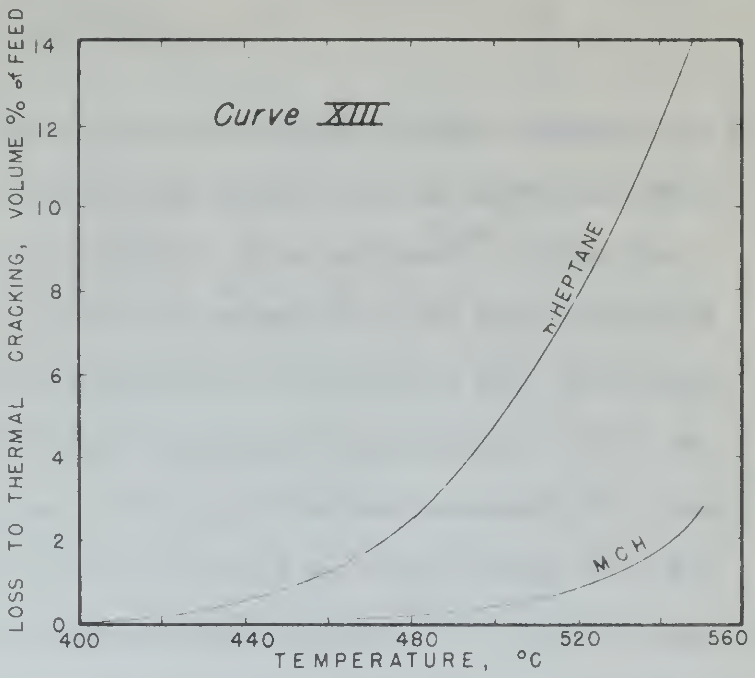
Effect of Ce and K Promoters



Effect of Temperature and Space Velocity on Catalyst Life

Curve XII, page 64, shows the effect of temperature and space velocity on the catalyst life. The feed was methyl cyclohexane and the catalyst used was number 150 (see Table III, page 57). The best curve is for a liquid hourly space velocity of 0.36 and a reaction temperature of 490° C. Keeping the space velocity substantially constant and varying the temperature results in a decrease in catalyst life for an increase in temperature, as shown for the two curves with a liquid hourly space velocity of 0.72 and reaction temperatures of 490° and 520° C, respectively. Increasing the space velocity has a marked effect on the catalyst life, as illustrated by the curve of liquid hourly space velocity 1.44 and reaction temperature 550°C. Such an increase in the space velocity appreciably lowers the life of the catalyst.

Curve XIII, page 66, illustrates the effect of thermal cracking on the raw feeds, normal heptane and methyl cyclohexane. The equipment used in the tests outlined above consisted of a stainless steel reaction chamber. Therefore, a thermal cracking test was made on the empty chamber to determine the amount of loss of feed by thermal cracking. It may be seen that the loss of normal heptane to thermal cracking at the reaction temperature of the above tests (490° C) is less than four per cent, and that of methyl



*Extent of Thermal Cracking in Stainless Steel Tubes*

cyclohexane is less than one-half of one per cent. Methyl cyclohexane permits far less loss to thermal cracking at elevated temperatures than does normal heptane. Nevertheless, the thermal cracking losses are all very low compared to the yields of toluene obtained.

Cerium-potassium-chromia-gamma alumina catalysts can be regenerated with hot air diluted with an inert gas such as flue gas at about 550° C. In a test run(3) a drop from eighty-eight per cent to seventy-four per cent conversion was noted after sixty-seven regenerations (400 processing hours) or an average decline per regeneration of 0.21 per cent conversion. The rate of decline decreased after that to an average of 0.12 per cent per regeneration after 200 regenerations (1200 processing hours). The ratio of processing time to the time required to completely remove the carbon deposit was about six to one for the cyclization of normal heptane, and twenty to one for the dehydrogenation of methyl cyclohexane. Table IV, page 68, will serve to illustrate this characteristic lower carbon deposition on the catalyst of methyl cyclohexane. For both catalysts, methyl cyclohexane had consistently lower rates of deposit than normal heptane, although the length of the run was ten hours, or two-thirds more than that of normal heptane.

TABLE IV(3)

Carbon Deposition

| Catalyst<br># | Type | feed | length of run hours | Carbon, weight % on cat. | of total feed |
|---|---|---|---|---|---|
| 167 | $Cr_2O_3$/gamma | MCH | 25 | 1.5 | 0.29 |
| 160 | Ce/K/$Cr_2O_3$/gamma | MCH | 25 | 1.1 | 0.17 |
| 167 | $Cr_2O_3$/gamma | $nC_7$ | 15 | 5.1 | 1.46 |
| 171 | Ce/K/$Cr_2O_3$/gamma | $nC_7$ | 15 | 3.1 | 0.68 |

It may therefore be seen that the properties of any particular catalyst may be varied over a wide range to meet certain operating conditions, and a special catalyst may well be developed to meet the requirements of any specific reaction. This discussion, of course, is not concerned with the economics of catalyst production and catalytic processes.

# CONCLUSIONS

While most of the toluene now made from petroleum is derived from the hydroforming process, any of the various processes described may be adapted to the production of toluene by proper selection of catalyst, feed stock and operating conditions. Feature of two or more processes may be combined. For example, developments may lead to a fluid-catalyst process which operates in an atmosphere of hydrogen, thus combining that process with the principles of hydroforming. Naturally, such developments involve complicated inter-relationships of patent rights.

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